JOURNAL OF CATALYSIS 8, 128-136 (1967)

Kinetics of the Vapor-Phase Oxidation of Methyl Alcohol on Vanadium Pentoxide Catalyst

S. K. BHATTACHARYYA, K. JANAKIRAM, AND N. D. GANGULY

From the Department of Applied Chemistry, Indian Institute of Technology, Kharagpur, India

Received October 3, 1966; revised January 3, 1967

The kinetics of oxidation of methanol was studied at 246°, 264°, and 281°C at low conversion in a flow reactor using vanadium pentoxide catalyst. The following rate equation, deduced assuming a steady state involving simultaneous reduction of catalyst by methanol and oxidation of the catalyst to the original state by gaseous oxygen, represents the experimental data satisfactorily

$$r = \frac{2k_1k_2P_mP_{O_2}}{k_1P_m + 2k_2P_{O_2}}$$

The activation energies of the two steps were, respectively, 7.5 and 9.0 kcal/mole. The data were also tested according to the following integrated equation:

$$\frac{V}{F} = -\frac{1}{k_1}\ln(1 - x) + \frac{1}{k_2}\ln\frac{2a}{2a - x}$$

INTRODUCTION

Formaldehyde, a very important chemical, is now prepared in industry by direct catalytic oxidation of methanol under controlled conditions, rather than by the alternative dehydrogenation process. Various advantages such as higher rate of reaction, easier temperature control, retention of catalytic activity for a longer time, and very high selectivity are achieved in the catalytic oxidation process. The undesirable degradation of methanol to carbon dioxide is checked by proper choice of catalyst and operating condition.

Much work has been done on the mechanism and kinetics of catalytic oxidation of methanol to formaldehyde, using almost exclusively silver oxide as the active catalyst component (*1–8*). But till now the mechanism of oxidation, especially in regard to the role of silver oxide, has not been unanimously settled.

Boreskov *et al.* (*9*) investigated the kinetics of methanol oxidation over Fe_2O_3–MoO_3 at 275°C and found the rate to be independent of oxygen and first order in methanol. The molar ratio of methanol to oxygen was below 0.5 in their experiments.

Recently Jiru, Wichterlova, and Tichy (*10*) have reported extensive work on the kinetics of oxidation of methanol to formaldehyde on iron oxide–molybdenum oxide catalyst. They have deduced a rate expression based on the mechanism which was originally suggested by Mars and van Krevelen (*11*) for the vapor-phase oxidation of aromatic hydrocarbons like benzene or napthalene on vanadium pentoxide. According to this mechanism, a steady state is assumed between the following two steps:

$$\text{Reactant} + (\text{Catalyst})_{\text{Ox}} = \text{Product} + (\text{Catalyst})_{\text{Red}} \quad (1)$$

$$(\text{Catalyst})_{\text{Red}} + O_2 = (\text{Catalyst})_{\text{Ox}} \quad (2)$$

A rate equation exactly similar to the one developed according to the above scheme can also be deduced from the modified Hinshelwood (*12*) mechanism. According to this concept adsorbed oxygen reacts with the other reactant remaining in the gaseous phase, and the rate of removal of adsorbed oxygen by reaction is equal to the rate of adsorption of oxygen.

Shelstad, Downie, and Graydon (*13*, *14*) studied the kinetics of oxidation of naphthalene and toluene and supported this modified Hinshelwood mechanism. Ioff *et al.* (*15*) also reported in favor of this theory.

Though both the mechanisms outlined above lead to the same rate expression, a very delicate but important point of difference exists between them. The first mechanism proposes the removal of actual lattice oxygen atoms by direct interaction with reductant, which must hence be chemisorbed, while the latter ignores such a catalyst–reductant interaction and instead, it suggests that only adsorbed oxygen molecules or atoms (and not the lattice oxygen) are removed by reacting with the reductant molecules, which remain exclusively in the gas phase.

Jiru *et al.* (*10*) carried out the oxidation at a high conversion level, which resulted in the formation of carbon monoxide, carbon dioxide, and methane. Moreover, for iron oxide–molybdenum oxide catalyst, though the nature of the active catalyst component was believed to be ferric molybdate, the exact relation between the composition and catalytic activity could not be ascertained. The disagreement between some of the results of Jiru *et al.* and those of Boreskov (*9*) is supposed to be due to this reason.

It is clear from the above discussion that serious indecision regarding the actual mechanism of oxidation of methanol is still left to be investigated and clarified. Hence the present investigation on the catalytic vapor-phase oxidation of methanol to formaldehyde was studied under a fairly wide range of operating conditions in order to throw light on the actual mechanism and also to derive a simple but accurate rate equation which might be used effectively for industrial reactor design. In order to avoid some complications mentioned earlier, the reaction was carried out at low conversions using vanadium pentoxide, a simple, well-studied, and active catalyst.

NOMENCLATURE

r	reaction rate (moles of HCHO/moles of CH_3OH sec cc)
P_m	partial pressure of methanol in feed (atm)
P_{O_2}	partial pressure of oxygen in feed (atm)
k_1	specific rate for reaction (1) (mole/mole sec cc atm)
k_2	specific rate for reaction (2) (mole/mole sec cc atm)
V	volume of catalyst bed (cc)
F	molal feed rate (mole/hr)
T	temperature (°C)
y	mole fraction of methanol
x	conversion (moles of methanol reacted/moles of methanol fed)
a	mole ratio of O_2/CH_3OH
Contact time, V/F	Reciprocal of space velocity and space velocity is expressed as the number of cc of the total feed at NTP per unit volume of catalyst per sec

Subscripts

m	methanol
O_2	oxygen

Greek Symbols

θ	fraction of the catalyst surface covered by oxygen
α	number of oxygen molecules needed to convert one molecule of methanol to formaldehyde.

EXPERIMENTAL

Apparatus. The flow diagram of the apparatus used for the present investigation is shown in Fig. 1. Compressed air from the cylinder (1) was passed through the purifying towers (2) containing fused calcium chloride, potassium hydroxide pellets, and active charcoal and metered through a flow meter (3) to the vaporizer (10). The pressure-compensator (4) was meant to nullify any pressure fluctuation in the flow line and the reactor. The feed rate of methanol was accurately controlled by the mercury displacement method, utilizing an arrangement almost like the one used by Griffith *et al.* (*16*). Stopcocks (8) and (9) were meant for feeding methanol and draining out mercury, respectively.

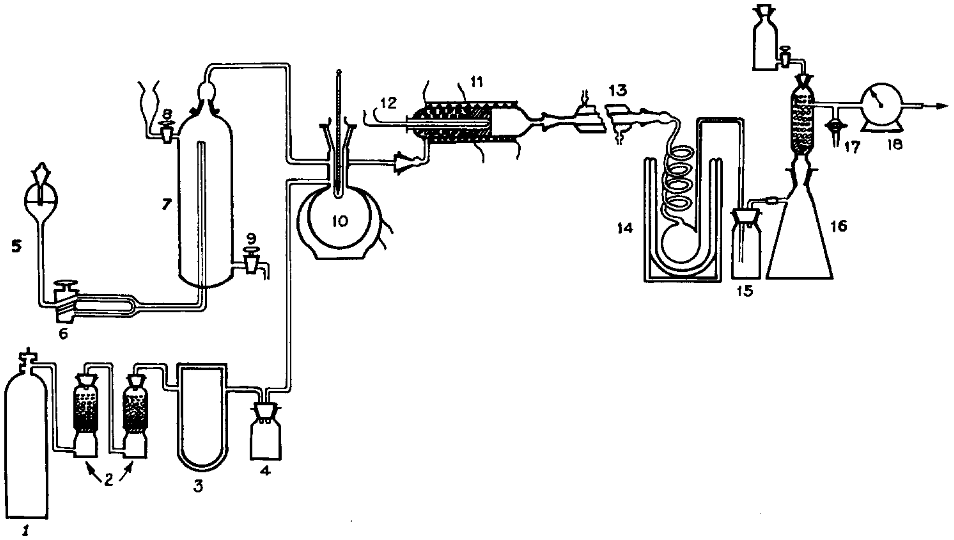

FIG. 1. Flow diagram of the apparatus.

In order to have a wide range of flow rates the reservoir (5) was connected to the feeder (7) by two different capillaries. By regulating the stopcock (6), the liquid could be fed to the evaporator through any one of the two capillaries. The vaporizer (10) was a 250-ml Pyrex flask having connections with the feeder, air cylinder, and reactor (11) and it was provided with a thermometer well. The flask was heated by a heating mantle and the temperature was controlled by a Sunvic Energy Regulator.

The reactor was made of Pyrex glass tube (1-inch diameter and 7 inches long). Another glass tube of 3-mm bore, sealed at one end and kept concentric with the reactor tube by means of a separable ground glass joint, was used for inserting the thermocouple (12). The reactor consisted of two sections—the preheater zone, filled with broken glass, and the catalyst zone. The catalyst was kept between two glass wool plugs. The two zones were heated by two separate tubular heaters controlled by variable transformers. The temperature of the reactor was measured by an accurately calibrated iron-constantan thermocouple.

The reaction products were passed through water (13) and ice-cooled (14) condensers, a water bubbler (15), and then through a washing tower arrangement (16). The exit gas was metered through a gas meter (18) and finally released to the atmosphere. Gas samples were collected intermittently through (17). All experimental runs were taken under steady state. For this purpose, a stream of reactants was passed over the catalyst at the required temperature for a period of 90 min. The products were then finally collected for another 30 min.

Material used. Methyl alcohol (A.R.) was kept over fused calcium chloride and distilled. The distilled methyl alcohol was diluted to 50% by volume.

Preparation and the physical characteristics of the catalyst. Vanadium oxalate, prepared by the addition of oxalic acid to a solution of ammonium metavanadate, was first dried and then decomposed to V_2O_5 at 400°C in a current of air. The surface area of the fresh catalyst, determined by the BET nitrogen adsorption method, was found to be 10.5 m^2/g. The pore-size distribution of the catalyst was measured by mercury porosimeter and the radius of 97.9% of the pores was above 729 Å. The total pore volume, determined by the Hg–He displacement method, was 0.6107 ml/g.

Analytical procedure. The experimental conditions were so chosen by preliminary investigation that formaldehyde was the only product. Neither carbon monoxide nor carbon dioxide was formed to any detectable extent.

Formaldehyde was estimated by the conventional argentometric method (*17*). The unconverted methanol was determined by oxidation with potassium dichromate, due correction being made for the presence of formaldehyde according to the following equations:

$$CH_3OH + K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 6H_2O + CO_2$$

$$3HCHO + 2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 11H_2O + 3CO_2$$

The accuracy of this analytical scheme was proved by taking known mixtures of methanol and formaldehyde and also by material balance.

Thermodynamic considerations. The free energy change (ΔG) and the equilibrium constant (K_p) of the reaction $CH_3OH(g) + \frac{1}{2}O_2(g) = HCHO(g) + H_2O(g)$ were calculated as functions of temperature, the necessary data being either collected from the literature or calculated by the group contribution method (*18*). The values of ΔG and K_p recorded in Table 1 indicate that the reaction is highly irreversible.

TABLE 1

THE VALUES OF ΔG AND K_p OF THE REACTION $CH_3OH(g) + \frac{1}{2}O_2(g) = HCHO(g) + H_2O(g)$ AT 1 ATMOSPHERE AND DIFFERENT TEMPERATURES

Temperature (°C)	$-(\Delta G)$ (kcal/g mole)	K_p
25°	42.900	3.4667×10^{31}
250°	44.068	2.8840×10^{18}
280°	44.084	2.8840×10^{17}
350°	44.594	4.7860×10^{15}
450°	43.125	1.8200×10^{12}

RESULTS AND DISCUSSION

Before starting the kinetic experiments, preliminary investigations on the diffusion characteristics of the catalyst were carried out to arrive at the condition where the diffusion resistances, both internal and external, would be negligible. For this purpose, the usual methods described by Corrigan *et al.* (*19*) were followed. From the variation of rate with the particle size of the catalyst and the volume of the catalyst, as shown in Figs. 2 and 3, it was concluded that the diffusion would be of very little importance with the catalyst particles within −150 + 170 BSS mesh size (0.104 to 0.089 mm) and at space velocities above 90 liters/hr ml.

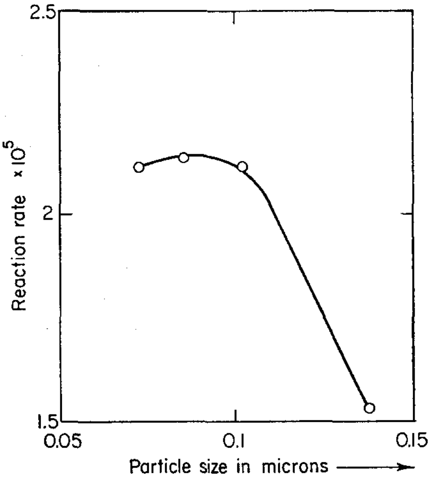

FIG. 2. Effect of particle size on reaction rate.

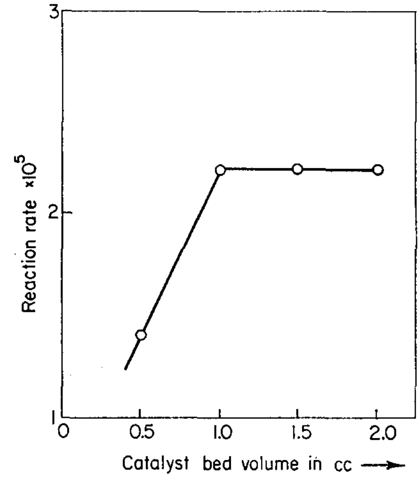

FIG. 3. Effect of bed volume on reaction rate.

It has been reported by the earlier workers (*20*, *21*) and also verified by actual industrial operation that an aqueous methanol feed is more conducive to higher yield, greater stability of the catalyst performance, and also for obtaining formaldehyde of desirable concentration. Hence in the present investigation the effect of water on the rate of conversion was studied (Fig. 4) and a mixture containing 50% by volume of methanol was used in all the kinetic experiments. This particular composition was considered to be the best compromise between the activity and stability of the catalyst. Moreover, the decomposition of methanol or formaldehyde could also be completely avoided under this condition. So the kinetic data obtained represented solely the main oxidation reaction and thus the interpretation became easier and more straightforward. Since the reaction was carried out at low conversion level (generally 5% to 10% of methanol fed) no correction was made for the volume change within the reactor. As shown in Fig. 4, the concentration of water in the feed was sufficiently high to ensure a steady level of oxidation rate. Several experiments were carried out to determine the noncatalytic rates of oxidation of methanol under the present range of experimental conditions and they were found to be negligible (6×10^{-7} moles/sec ml) compared to the catalytic rate. Hence, the catalytic rate was not corrected.

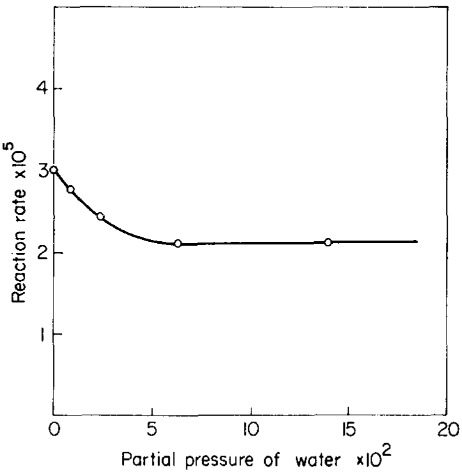

FIG. 4. Effect of water on reaction rate.

The rate of catalytic oxidation of methanol was determined as a function of the partial pressures of methanol and oxygen, and of the contact time, mainly at 281°C. A few rate measurements were also performed at 264°C and 246°C to determine the activation energy. The Figs. 5 and 6 represent the variation of rate with partial pressures of oxygen and methanol at 281°C.

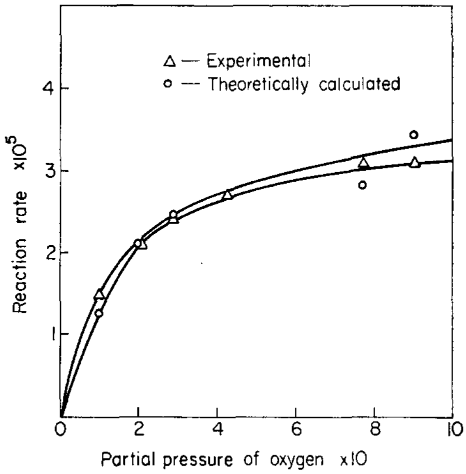

FIG. 5. Effect of partial pressure of oxygen on reaction rate: ○, experimental; △, theoretical.

The present kinetic data were critically examined in the light of the following mechanisms, the surface reaction in each case being assumed to be the rate-controlling step:

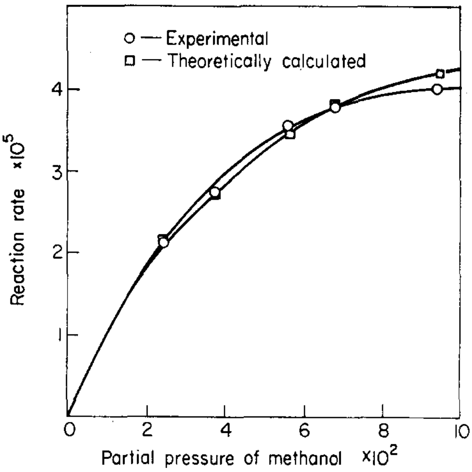

FIG. 6. Effect of partial pressure of methanol on reaction rate: ○, experimental; □, theoretical.

(1) reaction between atomically adsorbed oxygen and methanol in gas phase;
(2) reaction between molecularly adsorbed oxygen and methanol in gas phase;
(3) reaction between adsorbed methanol and atomically adsorbed oxygen:

(4) reaction between methanol and molecular oxygen, both being adsorbed.

All except the first scheme led to one or more negative coefficients in the rate equation (as found by least-squares calculations) and hence were rejected outright. Though the equation derived from mechanism (1) had all the coefficients positive, it could not satisfactorily represent the experimental data throughout the entire range. Moreover, the exact physical interpretations of the coefficients proved to be difficult.

Finally, the kinetic expression derived by Mars and van Krevelen (*11*) on the basis of the oxidation–reduction mechanism, which has already been discussed, was tested.

Assuming first order dependence of the rate of reaction (1) (i.e., reduction of the catalyst by methanol) on the partial pressure of methanol

$$-dP_m/dt = k_1 P_m \theta, \tag{3}$$

where θ is the fraction of the surface occupied by oxygen.

With similar assumption as before, the rate of the second step (i.e., the oxidation of the catalyst by oxygen) may be represented as

$$-dP_{O_2}/dt = k_2 P_{O_2}(1 - \theta) \tag{4}$$

Under steady state

$$\alpha(dP_m/dt) = dP_{O_2}/dt \tag{5}$$

where α is the number of oxygen molecules required for converting one methanol molecule to formaldehyde.

Hence from Eqs. (3), (4), and (5)

$$\alpha k_1 P_m \theta = k_2 P_{O_2}(1 - \theta)$$

or

$$\theta = \frac{k_2 P_{O_2}}{k_2 P_{O_2} + \alpha k_1 P_m} \tag{6}$$

Substituting the values of θ in Eq. (3)

$$r = \frac{k_1 k_2 P_m P_{O_2}}{k_2 P_{O_2} + \alpha k_1 P_m} = 1 \Big/ \left(\frac{1}{k_1 P_m} + \frac{\alpha}{k_2 P_{O_2}}\right) \tag{7}$$

It is, of course, possible to derive a more generalized rate equation like Eq. (6) when no restrictive assumptions regarding the order of the reaction with respect to the reactants are imposed

$$r = \frac{k_1 k_2 P_m{}^a P_{O_2}^b}{k_2 P_{O_2}{}^b + \alpha k_1 P_m{}^a} \tag{8}$$

The values of exponents a and b, can be evaluated graphically, from the variation of rate with the partial pressure of one of the reactants, keeping that of the other constant. But, fortunately for the present case, it will shortly be proved that Eq. (7) represented the kinetic data with excellent accuracy.

From Eq. (7)

$$\frac{1}{r} = \frac{1}{k_1 P_m} + \frac{\alpha}{k_2 P_{O_2}} \tag{9}$$

Therefore, at constant P_{O_2}

$$\left(\frac{1}{r}\right) P_{O_2} = A + \frac{1}{k_1 P_m} \tag{9a}$$

and at constant P_m

$$\left(\frac{1}{r}\right) P_m = A' + \frac{\alpha}{k_2 P_{O_2}} \tag{9b}$$

where

$$A = \frac{\alpha}{k_2 (P_{O_2})_{\text{constant}}}, \qquad A' = \frac{1}{k_1 (P_m)_{\text{constant}}}$$

So, according to (9a) and (9b), the plots of $(1/r)P_{O_2}$ against $1/P_m$ and $(1/r)P_m$ against $1/P_{O_2}$ should be linear, as shown in Figs. 7 and 8. This definitely shows the validity of

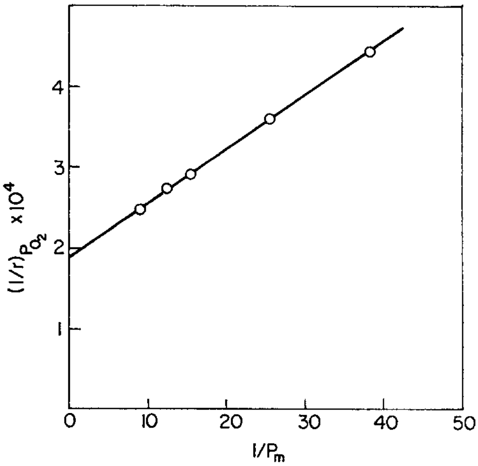

FIG. 7. Plot of $(1/r)P_{O_2}$ vs. $1/P_m$.

the rate equation (7) as well as of the assumptions regarding the order of reaction.

Assuming $\alpha = 0.5$, the values of the rate constants k_1 and k_2 at 281°C were calculated by the method of least squares and also graphically by utilizing Eqs. (9a) and (9b) and they agreed very well. The values for k_1 and k_2 (calculated by least-square method) at three temperatures are recorded in Table 2.

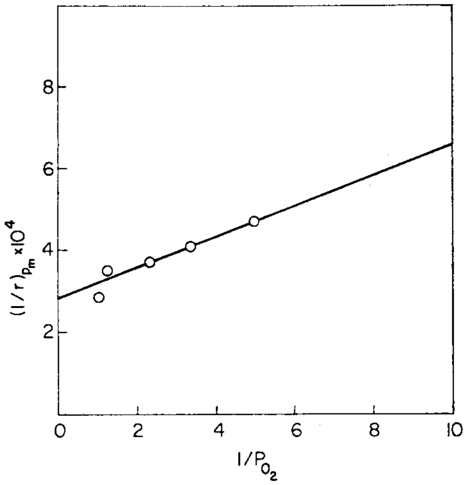

FIG. 8. Plot of $(1/r)P_{O_2}$ vs. $1/P_{O_2}$.

The least-square values of k_1 (1.55×10^{-3} mole/mole sec cc atm) and k_2 (11×10^{-5} mole/mole sec cc atm) at 281°C were used in Eq. (7) to draw the theoretical rate curves which coincided excellently with the experimental curves as shown in Figs. 5 and 6.

The activation energies of the overall process and also of the individual steps were evaluated from the usual Arrhenius plots as shown in Fig. 9 and they are recorded in Table 2.

From the relative magnitudes of k_1 and k_2, it may be surmised that the overall rate of oxidation of methanol would be influenced more by the second step than by the first.

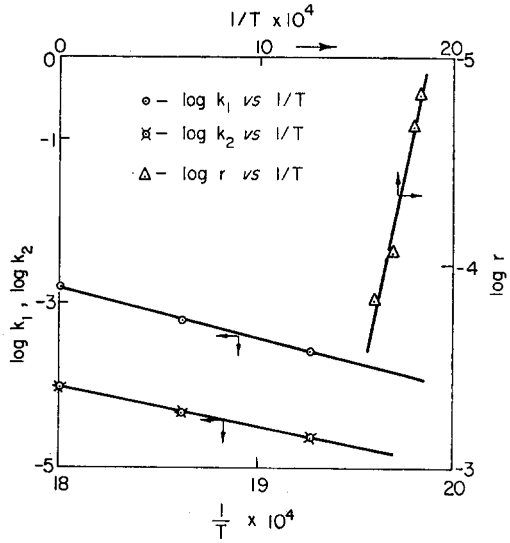

FIG. 9. Arrhenius plots: ⊙, log k_1 vs. $(1/T) \times 10^4$; ⌘, log k_2 vs. $1/T \times 10^4$; △, log r vs. $(1/T) \times 10^4$.

The effect of contact time (V/F) on methanol oxidation was studied and the results are shown in Table 3. These data were tested in the light of the integrated form of Eq. (7) derived below:

$$r = \frac{2k_1k_2P_mP_{O_2}}{k_1P_m + 2K_2P_{O_2}}$$

$$\frac{1}{r} = \frac{1}{k_1P_m} + \frac{1}{2k_2P_O}$$

In a flow reactor

$$\frac{V}{Fy} = \int_0^x \frac{dx}{r}$$

where x is the fractional conversion of CH_3OH; r, the moles of CH_3OH converted/hr; and y, the mole fraction of

TABLE 2

THE VALUES OF k_1, k_2 AND ACTIVATION ENERGIES

	246°C	264°C	281°C	Activation energy (kcal/g mole)
k_1	0.30×10^{-3}	0.60×10^{-3}	1.55×10^{-3}	7.5
k_2	2.62×10^{-5}	4.97×10^{-5}	11.00×10^{-5}	9.0
r^a	—	—	—	8.0

[a] r measured at $P_m = 0.026$, $P_{O_2} = 0.2$, S.V. = 90 liters/hr cc.

TABLE 3

VARIATION OF CONVERSION WITH CONTACT TIME

Mole ratio of O_2/CH_3OH 6.9875
Mole ratio of O_2/N_2 0.2500
Mole fraction of CH_3OH 0.2800
Reaction temperature 281°C
Catalyst bed volume 1.2 cc

$$k_1 = 1.55 \times 10^{-3} \frac{\text{mole}}{\text{mole sec cc atm}}$$

$$k_2 = 11 \times 10^{-5} \frac{\text{mole}}{\text{mole sec cc atm}}$$

Sl. No.	Contact time (hr)	Conversion of methanol (x, moles/hr)	Total molal feed/hr	V/F Exptl.	V/F Calc.
1	4.00×10^{-5}	0.3219	1.3380	0.8962	0.8469
2	2.00×10^{-5}	0.1784	2.6670	0.4483	0.4321
3	1.34×10^{-5}	0.1304	4.0150	0.2989	0.3084
4	0.89×10^{-5}	0.0829	6.0220	0.1993	0.2004
5	0.67×10^{-5}	0.0430	8.0310	0.1494	0.1394

Standard deviation, ±0.03

methanol. Substituting for the value of r we obtain

$$\frac{V}{F} = y \int_0^x \left(\frac{1}{k_1 P_m} + \frac{1}{2k_2 P_{O_2}} \right) dx$$

The partial pressures of methanol and oxygen may be expressed as

$$P_m = P_T y(1 - x)$$
$$P_{O_2} = P_T y a - \tfrac{1}{2} P_T y x = P_T y(a - \tfrac{1}{2}x)$$

where $P_T = 1$ atm and a is the mole ratio of O_2 to CH_3OH.

$$\begin{aligned} \frac{V}{F} &= y \int_0^x \frac{dx}{k_1 y(1 - x)} + y \int_0^x \frac{dx}{2k_2 y(a - \frac{1}{2}x)} \\ &= \frac{1}{k_1} \int_0^x \frac{dx}{(1 - x)} + \frac{1}{k_2} \int_0^x \frac{dx}{(2a - x)} \\ &= -\frac{1}{k_1} \ln(1 - x) + \frac{1}{k_2} \ln \frac{2a}{(2a - x)} \qquad (10) \end{aligned}$$

The theoretical values of V/F for different conversions were calculated with the values of k_1 and k_2 (same as those used in differential rate equation) as shown in Table 3. There was good agreement between theoretically and experimentally calculated values of V/F, as shown in Table 3.

As regards the choice between van Krevelen's mechanism and the modified Hinshelwood mechanism, the present authors favor the former on the basis of the following reasons:

Tarama *et al.* (*22*) by X-ray diffraction have established that certain V–O distances in V_2O_5 lattice (exposed on the 001 face) are comparable in length with those in $VOCl_3$, having a double bond between oxygen and vanadium. According to them, these oxygen atoms are more reactive (especially in the presence of easily oxidizable compounds) since they are linked with bonds having appreciable "double bond characteristics."

It has been observed by the present authors that the color of vanadium pentoxide catalyst became black (characteristic of lower oxides of V) when only methanol was allowed to pass over it for a short time. It was proved that the black color was not due to carbon deposition because carbon dioxide could not be detected in the exit gas of the regenerating cycle. That the lattice oxygen from V_2O_5 is removed during the oxidation of organic compounds and also that a lower oxide of vanadium (supposed to be $V_2O_{4.34}$) is the actual catalyst composition of V_2O_5 has been suggested by various workers (*23*, *24*, *25*). The higher activity of the oxygen-deficient V_2O_5 (partially reduced) is also expected from its well-known *n*-type conductivity. Jiru *et al.* have also found a remarkable equality between the amount of oxygen removed by methanol (in the absence of oxygen in the gas phase) and the oxygen taken up subsequently by the reduced catalyst.

It is, of course, true that in spite of all these observations, one cannot make an absolute choice between the above two mechanisms. It appears that to arrive at a definite conclusion, detailed and accurate kinetic studies on the reaction and isotope exchange with a specially prepared V_2O_5 catalyst, containing a sufficient concentration of O^{18} in the lattice, must be carried out.

Finally, the rate equation derived here correlates the kinetic data nicely within the low-conversion range studied. A detailed investigation on the kinetics of methanol oxidation at high conversion level is in progress.

REFERENCES

1. ALROSHANKO, V. I., AND KUSHNENKO, I. P., *Int. Chem. Eng.* 4, 581 (1960).

2. Hader, R. N., Wallace, R. D., and Mekinney, R. W., *Ind. Eng. Chem* **44,** 1588 (1952).
3. Planovskya, I. P., and Γopechieve, K. V., *Kinetics & Catalysis* (USSR) (Engl. Transl.) **2,** 375 (1961).
4. Vladovets, I. N., and Pshezhetskii, S. Ya., *Zh. Fiz. Khim* **25,** 612 (1951).
5. Poposkii, V. V., Boreskov, G. B., and Muzykantov, V. S., *Zh. Fiz. Khim* **35,** 192 (1961).
6. Winters, F. R. S., *Advan. Catalysis* **10,** 196 (1958).
7. Royton, V. A., *Actes Congr. Intern. Catalyse 2^{e}, Paris* **1,** 759 (1960).
8. Vasilev, V. N., Elovich, S. Y., and Margolis, L. Ya., *Dokl. Akad Nauk SSSR* **101,** 703.
9. Boreskov, G. K., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1,** 213 (1965).
10. Jiru, P., Wichterlova, B., and Tichy, J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1,** 199 (1965).
11. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci.* **3** (special supplement on the proceedings of the Conference on Oxidation Process), p. 41 (1954).
12. Hinshelwood, C. N., "The Kinetics of Chemical Change," p. 207. Oxford Univ. Press, London, 1940.
13. Shelstad, K. A., Downie, J., and Graydon, W. F., *Can. J. Chem. Eng.* **35,** 102 (1960).
14. Downie, J., Shelstad, K. A., and Graydon, W. F., *Can. J. Chem. Eng.* **39,** 201 (1961).
15. Ioffe, I. I., and Lyubarskii, A. G., *Kinetica i Kataliz* **3,** 261 (1962) [Abstract, *J. Catalysis* **1,** 397 (1962)].
16. Grifith, R. H., Marsh, J. D., and Martin, M. J., *Proc. Roy. Soc. (London)* **A224,** 426 (1954).
17. Siggia, S., "Quantitative Organic Analysis via Functional Groups," p. 32. Wiley, New York, 1949.
18. Hougen, O. A., Watson, K. M., and Ragatz, R. A., "Chemical Process Principles," Part II, p. 1004. Asia Publishing House, Bombay, India.
19. Corrigan, T. E., *Chem. Eng.* **62,** 199 (1955).
20. Walker, Fredric J., "Formaldehyde," p. 9. Reinhold, New York, 1953.
21. Uhl, H. B., and Cooper, I. H., U. S. Patent 2,465,498 (1949).
22. Tarama, K., Taranishi, S., Yoshida, S., and Tamura, N., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1,** 282 (1965).
23. Berets, D. J., and Clark, H., *Advan. Catalysis* **9,** 204 (1956).
24. Bhattacharyya, S. K., and Gulati, I. B., *Ind. Eng. Chem.* **50,** 1719 (1958).
25. Simard, G. L., Segel, J. F., Arnot, R. J., and Siegel, L. A., *Ind. Eng. Chem.* **47,** 1424 (1953).